

## Supporting Information

# Solid-State Thin-Film Supercapacitors with Ultrafast Charge/Discharge Based on N-Doped-Carbon-Tubes/Au-Nanoparticles-Doped-MnO<sub>2</sub> Nanocomposites

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## 1. Experimental section

### Preparation of ZnO/N-doped-C nanorods

The preparation of ZnO/N-doped-C nanorods grown on carbon fabric were described as follows: First, the carbon fabric was cleaned by sonication in ethanol, followed by deionized water, which was used as a substrate for ZnO nanorods by the hydrothermal synthesis method.<sup>1</sup> Next, the substrate was immersed in 5 mM zinc acetate-ethylene

glycol monomethyl ether colloidal solution for 30 min, and then thermal treatment was given at 300 °C for 10 min. This procedure was repeated three times, and thermal decomposition of zinc acetate formed ZnO nanocrystals on the substrate as seeds for subsequent ZnO nanorods growth. The seeded substrate was then placed in 45 mL of the growth solution, which consisted of 0.05 M zinc nitrate and 0.05 M hexamethylenetetramine. Thereafter, the container was heated at a constant temperature of 95 °C for 8 h in an oven. Finally, the carbon fabric grown with ZnO nanorods was washed with deionized water and dried in air. The carbon fabric grown with ZnO nanorods was then dipped into a dilute aqueous solution of dopamine, buffered to a pH typical of marine environments (2 mg of dopamine per milliliter of 10 mM tris, pH 8.5) for 12 h. Finally, the carbon fabric/ZnO covered with a polymer film was dried, and thermal treatment was given at 500 °C under Ar atmosphere with a heating rate of 20 °C min<sup>-1</sup> for 3 h, forming the ZnO/N-doped-C heterstructured nanorod arrays on the carbon fabric.

### **Preparation of Fe<sub>2</sub>O<sub>3</sub> nanorods**

Fe<sub>2</sub>O<sub>3</sub> nanorods were synthesized by a previously reported method.<sup>2</sup> In brief, a cleaned carbon fabric (1×2 cm<sup>2</sup>) was immersed into 40 mL of the precursor solution, which consisted of 0.15 M ferric chloride and 1 M sodium nitrate. The solution pH was adjusted to about 1.5 using HCl. The container was heated at a constant temperature of 95 °C for 16 h in an oven, and then allowed to cool to room temperature. A uniform yellow layer of akaganeite ( $\beta$ -FeOOH) nanorod film was obtained on the carbon fabric, washed with deionized water, and dried in air. The as-prepared FeOOH samples were then further thermally annealed at 400 °C under Ar atmosphere for 1 h. The mass of the Fe<sub>2</sub>O<sub>3</sub> was 4.63 mg/cm<sup>2</sup>.

### **Fabrication of N-doped-carbon-tubes/Au-nanoparticles-doped-MnO<sub>2</sub> (NCTs/ANPDM) and NCTs/MnO<sub>2</sub> nanocomposites**

The N-doped-carbon-tubes/Au-nanoparticles-doped-MnO<sub>2</sub> nanocomposite was synthesized using an alternant cyclic voltammetry. First, the ZnO/N-doped-C

nanorods coated carbon fabric was used as the working electrode ( $1 \times 1 \text{ cm}^2$ ), Pt gauze ( $1 \times 1.5 \text{ cm}^2$ ) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammograms were recorded between 0.4 and 1.3 V (vs. SCE) in an aqueous solution containing 0.05 M  $\text{Mn}(\text{Ac})_2$  and 0.1 M  $\text{Na}_2\text{SO}_4$ . Subsequently, the ZnO/N-doped-C/ $\text{MnO}_2$  electrode was deposited with gold in an aqueous solution containing 3 mM  $\text{HAuCl}_4$  and 0.1 M KCl, which resulted in a new ZnO/N-doped-C/ $\text{MnO}_2$ -Au electrode. The two steps were repeated five times, and the ZnO-nanorods/N-doped-C/ANPDM electrode was prepared. Finally, the ZnO-nanorods/N-doped-C/ANPDM electrode was dipped into 3.0 M KOH solution to etch the ZnO nanorod templates to form NCTs/ANPDM electrode. For comparison, the NCTs/ $\text{MnO}_2$  electrode was also prepared under the same experimental condition. The key step for the fabrication is to adjust the scan rate and control the total electric quantity for each deposition. The active materials of the NCTs/ANPDM and NCTs/ $\text{MnO}_2$  electrodes are  $0.27 \text{ mg/cm}^2$  and  $0.21 \text{ mg/cm}^2$ , respectively.

### **Preparation of the PVA-LiCl electrolyte**

The PVA-LiCl electrolyte was prepared as follows: 1.696 g of LiCl was added into 40 mL of deionized water, and then 4 g of PVA power was added. The mixture was heated steadily to  $95^\circ\text{C}$  under vigorous stirring until the solution became clear. Then, the solution was kept at  $95^\circ\text{C}$  without stirring. The ionic conductivity of the PVA-LiCl electrolyte films was determined by measuring the impedance response of the test cell ( $1 \times 1 \text{ cm}^2$ ) using a ST2258A multifunctional digital four-probe tester (Suzhou Jingge Electronic Co., LTD) over the frequency range 1 Hz to 1 MHz. The ionic conductivity of the PVA-LiCl electrolyte is  $5.5 \times 10^{-3} \text{ S cm}^{-1}$  at room temperature.

### **Assembly of the devices**

**SSC device** The solid-state symmetric supercapacitor was assembled with two pieces of NCTs/ANPDM electrodes ( $1 \times 2 \text{ cm}^2$ ) with an electrolyte-soaked separator (filter paper with  $8 \mu\text{m}$ ) in between. Prior to the assembling, the NCTs/ANPDM electrodes

were immersed in the PVA-LiCl gel solution for 5 min, respectively. They were then assembled and kept at room temperature. After the PVA-LiCl gel solidified, the solid-state supercapacitor was prepared.

**ASC device** The solid-state asymmetric supercapacitor was assembled with NCTs/ANPDM electrode and Fe<sub>2</sub>O<sub>3</sub>-nanorods electrode (1×2 cm<sup>2</sup>) with an electrolyte-soaked separator (filter paper with 8 μm) in between. Prior to the assembling, the NCTs/ANPDM electrode and Fe<sub>2</sub>O<sub>3</sub> nanorods electrode were immersed in the PVA-LiCl gel solution for 5 min, respectively. They were then assembled and kept at room temperature. After the PVA-LiCl gel solidified, the solid-state supercapacitor was prepared.

### **Electrochemical measurements**

All the electrochemical measurements were conducted using an electrochemical work-station (CHI760E). The electrochemical studies of single electrodes were performed in a three-electrode configuration, with a Pt gauze counter-electrode and a SCE reference electrode, in 1.0 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution.

### **Characterizations**

Materials morphology and crystal structure of the as-prepared electrodes were conducted by field-emission scanning electron microscope (FESEM, FEI, Nova NanoSEM 450) and transmission electron microscope (TEM, FEI, Tecnai G20, 200 kV). The chemical composition and oxidation status of the samples were analyzed using X-ray diffractometer (XRD, X' Pert PRO, Panalytical B.V., Netherlands) and X-ray photoelectron spectroscope (XPS, VG Multilab 2000).

## **2. Electrochemical characterization and analysis**

The mass of MnO<sub>2</sub> or Au of the electrodes was calculated using the following equation (1):

$$m = \frac{Q}{nF} \times Mr \quad (1)$$

where  $m$  is the mass of  $\text{MnO}_2$  or Au (in g);  $Q$  is the total electric quantity (C) for each deposition measured by cyclic voltammetry with three electrodes;  $n$  is the charge transfer number;  $F$  is the Faradic constant (in  $F$ ); and  $Mr$  is the relative molecular mass or atomic mass.

The specific capacitance of the single electrode based on active material was calculated from CV and GCD curves, respectively, according to the following equations:

$$C_m = \frac{\int_a^b I(V) dV}{\Delta V \times \nu \times m} \quad (2)$$

$$C_m = \frac{I \times \Delta t}{m \times \Delta V} \quad (3)$$

where the  $\int_a^b I(V) dV$  is the integrated area of the CV curve in one cycle;  $\nu$  is the scan rate;  $I$  is the constant discharge current;  $\Delta t$  is the time for a full discharge;  $m$  is the net mass of active material; and  $\Delta V$  is the voltage drop on discharge (excluding the  $V_{\text{drop}}$ ).

Regarding the SSC, the solid-state SSC was assembled with two pieces of the same NCTs/ANPDM electrodes and the specific capacitance of the device based on active material was calculated from galvanostatic charge/discharge curves according to the following equation:<sup>3-4</sup>

$$C_{\text{device}} = 2 \times \frac{I \times \Delta t}{m \times \Delta V} \quad (4)$$

where  $I$  is the constant discharge current;  $\Delta t$  is the time for a full discharge;  $m$  is the mass of active materials in one working electrodes; and  $\Delta V$  is the voltage drop on discharge (excluding the  $V_{\text{drop}}$ ).

Regarding the ASC, the solid-state SSC was assembled with NCTs/ANPDM electrode (positive) and  $\text{Fe}_2\text{O}_3$  nanorods electrode (negative). The charge balance will follow the relationship  $q^+ = q^-$ . The charge stored by each electrode depends on the

capacitance ( $C_m$ ), the potential range for the charge/discharge process ( $\Delta E$ ), and the mass of the active materials ( $m$ ) following the formula:

$$q = C_m \times \Delta E \times m \quad (5)$$

In order to get  $q^+ = q^-$  at 5 mV/s, the mass balance between NCT/ANPDM and  $\text{Fe}_2\text{O}_3$  will be calculated as follows:

$$\frac{m_{\text{NCT/ANPDM}}}{m_{\text{Fe}_2\text{O}_3}} = \frac{C_{\text{Fe}_2\text{O}_3} \times \Delta E_{\text{Fe}_2\text{O}_3}}{C_{\text{NCT/ANPDM}} \times \Delta E_{\text{NCT/ANPDM}}} \approx \frac{1}{17.3}$$

Therefore, the calculated weight ratio between the NCT/ANPDM electrode and  $\text{Fe}_2\text{O}_3$  electrode is about 1:17.3.

The specific capacitance of the ASC was calculated from galvanostatic charge/discharge curves according to the following equation:<sup>5</sup>

$$C_{\text{device}} = \frac{I \times \Delta t}{\Delta V \times m} \quad (6)$$

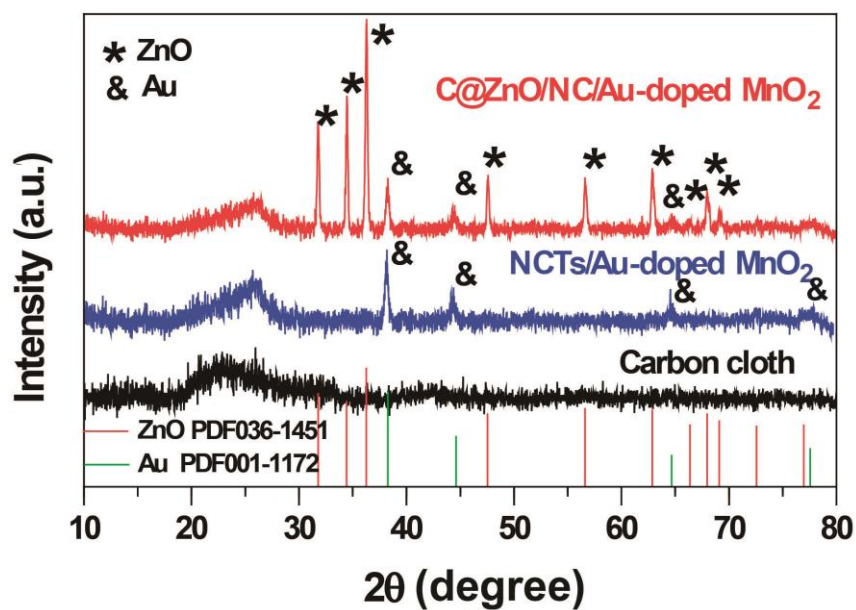
where  $I$  is the constant discharge current;  $\Delta t$  is the time for a full discharge;  $m$  is the total mass of active materials in the two working electrodes; and  $\Delta V$  is the voltage drop on discharge (excluding the  $V_{\text{drop}}$ ).

The gravimetric energy density ( $E$ ) and power densities ( $P$ ) against two electrodes in the device were calculated using the following formulas:<sup>5</sup>

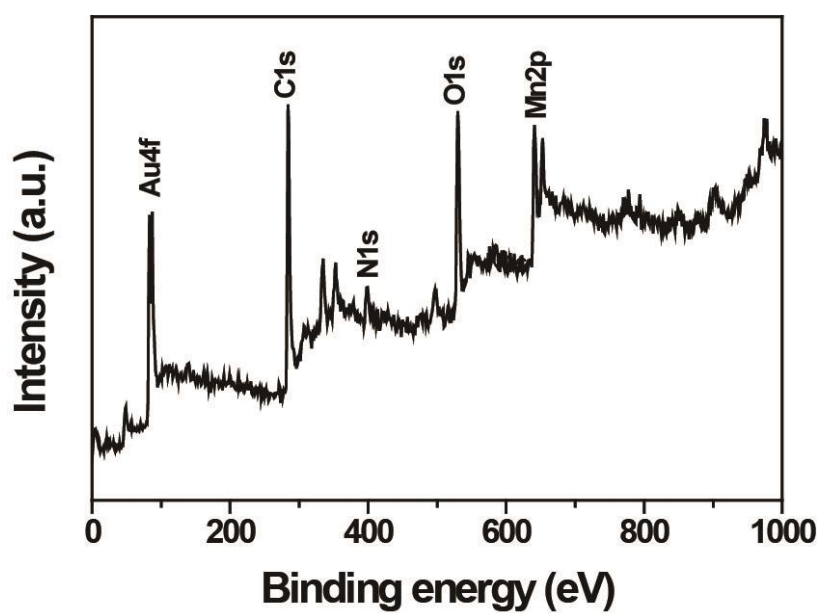
$$E = \frac{C_{\text{device}} V^2}{2} \times \frac{1}{3600} \quad (7)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (8)$$

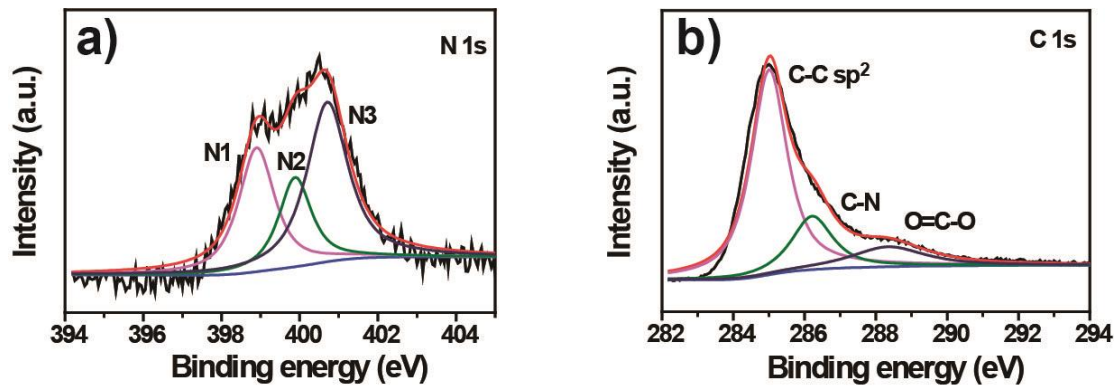
where  $V$  is the operating voltage (obtained from the discharge curve subtracted by the  $V_{\text{drop}}$ );  $C_m$  is the total capacitance of the device; and  $\Delta t$  is the time for a full discharge.



**Figure S1.** XRD of the as-prepared NCTs/ANPDM electrode.



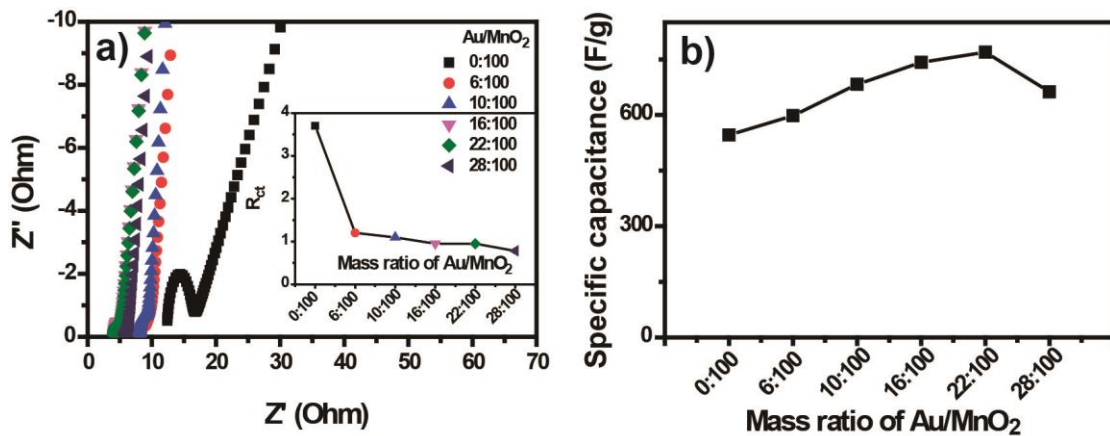
**Figure S2.** XPS survey for a NCTs/ANPDM nanocomposite electrode.



**Figure S3.** XPS in the region of N 1s (a) and C 1s (b) orbits (“black” represents the raw data, and the red line is the total fitted curve) for NCTs/ANPDM nanocomposite.

**Table S1.** The fractions of the oxygen bonding states calculated from the XPS O 1s peaks of NCTs/ANPDM

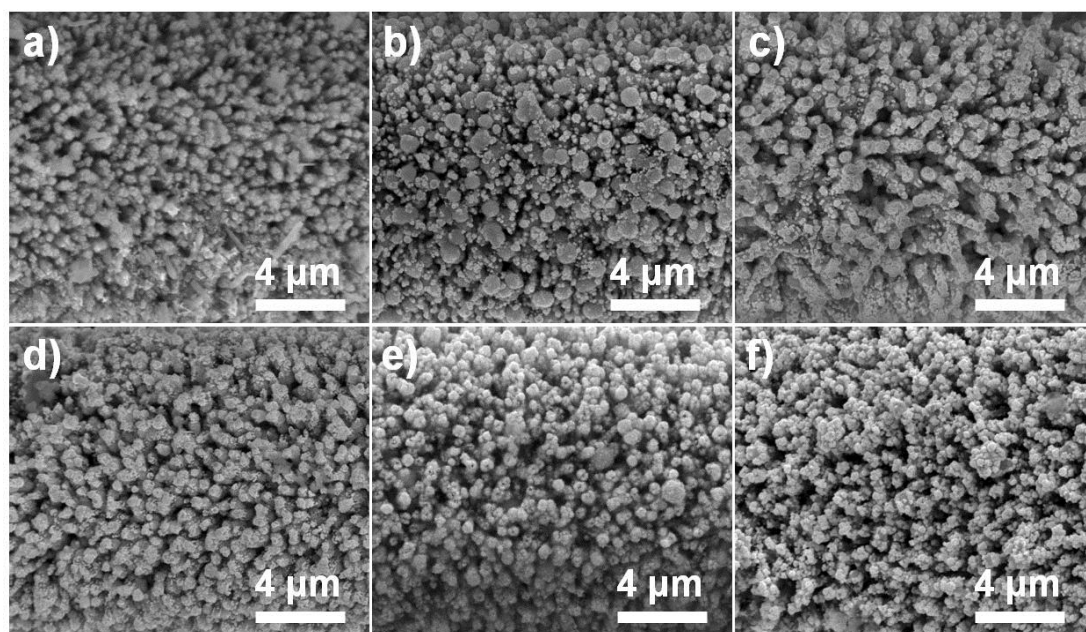
Samples	Mn 2p (eV)			O 1s (eV)		
	2p <sub>3/2</sub>	2p <sub>1/2</sub>	Δ BE		BE (eV)	Area%
NCTs/ANPDM	641.6	653.6	12.0	Mn-O-Mn	529.8	20.4
	643.1		10.5	Mn-O-H	530.3	21.0
				H-O-H	531.2	20.6
				O-C-O	532.0	20.9
				O=C-O	533.3	17.1



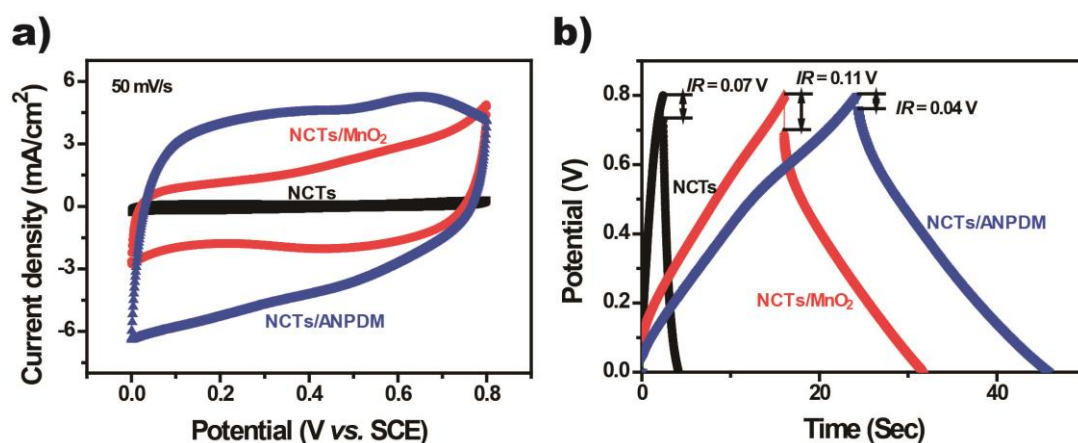
**Figure S4.** The influence of the Au/MnO<sub>2</sub> weight ratio in the NCTs/ADPDM



nanocomposite. (a) EIS of Nyquist plots for the NCTs/ANPDM electrodes with different Au/MnO<sub>2</sub> weight ratio. (b) The specific capacitance of the NCTs/ANPDM nanocomposites with different Au/MnO<sub>2</sub> weight ratio at scan rate of 50 mV/s.

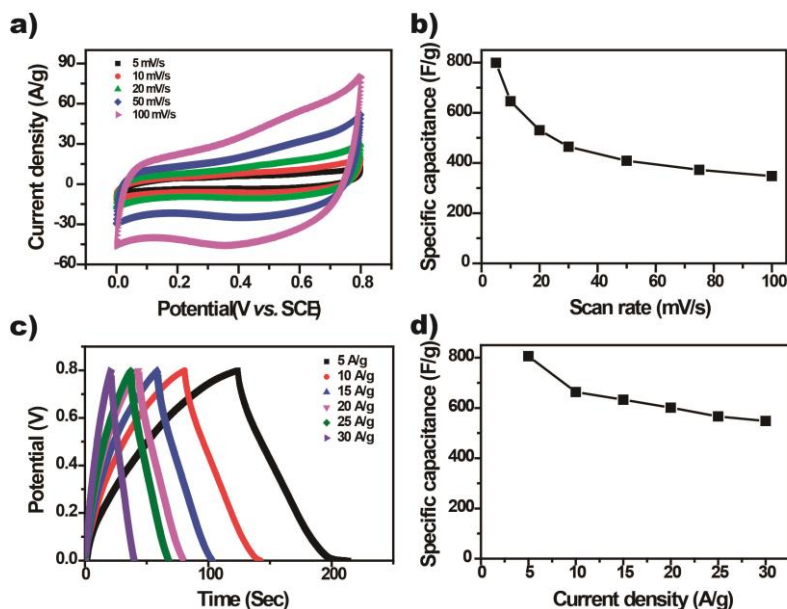


**Figure S5.** SEM images of the top view of NCTs/ANPDM nanocomposite with different Au/MnO<sub>2</sub> weight ratio, (a) 0:100; (b) 6:100; (c) 10:100, (d) 16:100; (e) 22:100; (f) 28:100, which were controlled by the deposition electric quantity.

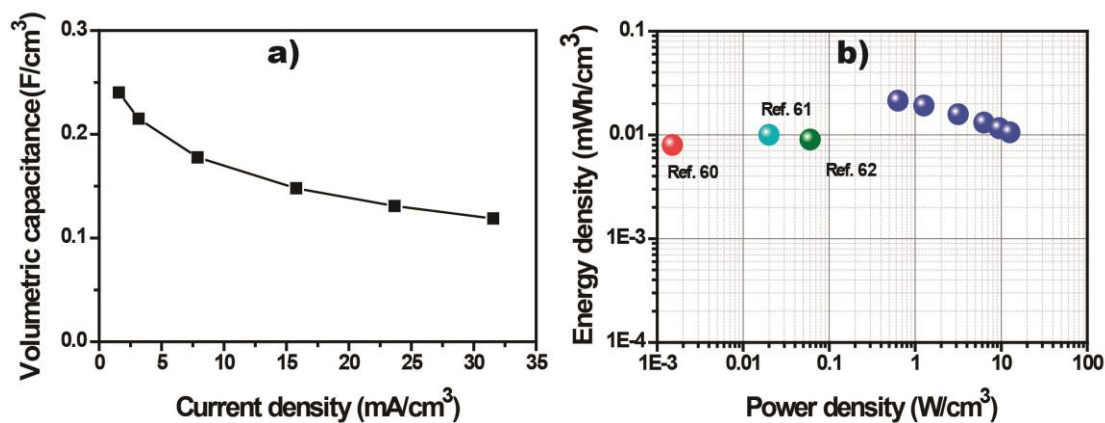


**Figure S6.** a) CV curves for NCTs, NCTs/MnO<sub>2</sub>, NCTs/ANPDM electrodes at the same scan rate (50 mV/s) in 1.0 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. b) Galvanostatic

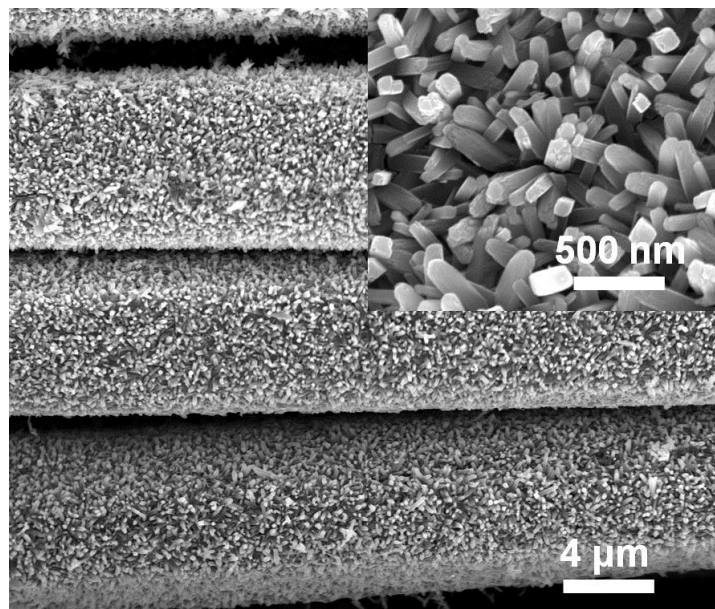
charge-discharge curves of NCTs, NCTs/MnO<sub>2</sub>, and NCTs/ANPDM electrodes collected at the same current density.



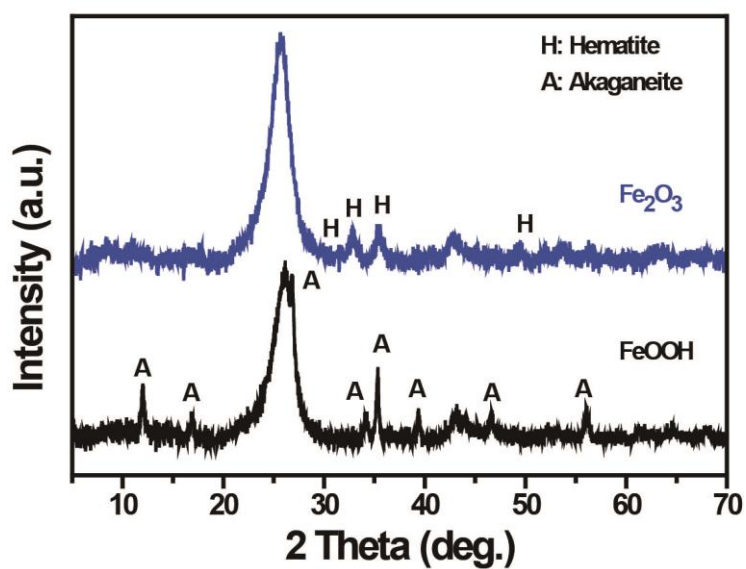
**Figure S7.** a) CV curves for NCTs/MnO<sub>2</sub> electrode at different scan rates in 1.0 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. b) Mass-specific capacitance of NCTs/MnO<sub>2</sub> electrode calculated from CV curves as a function of scan rate. c) Galvanostatic charge-discharge curves of NCTs/MnO<sub>2</sub> electrode collected at different current densities. d) Mass-specific capacitance of NCTs/MnO<sub>2</sub> electrode calculated from GCD curves as a function of current densities.



**Figure S8.** a) Volume specific capacitance of the solid-state SSC device calculated from GCD curves as a function of current densities. b) Ragone plots of the solid-state SSC device.

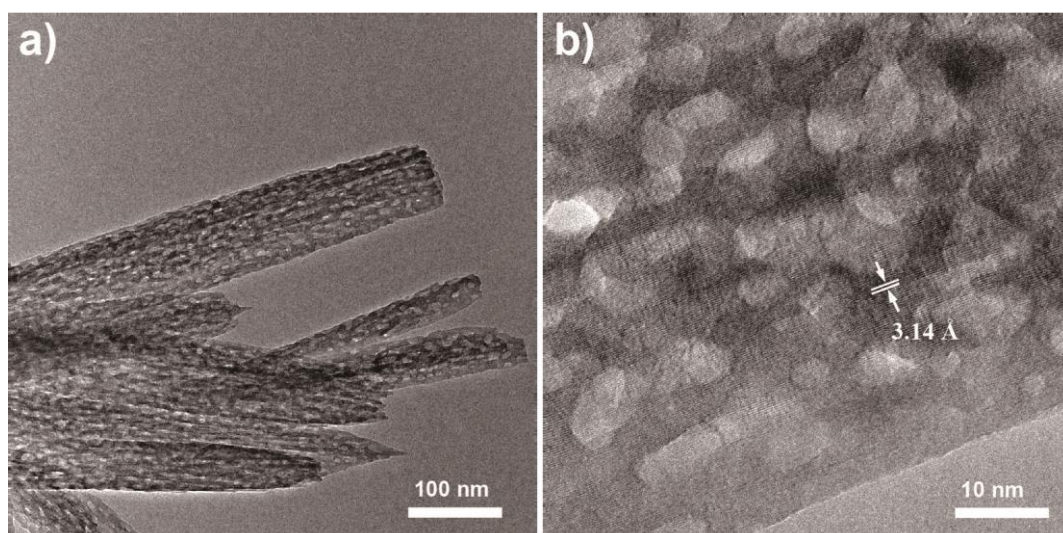


**Figure S9.** SEM image of the Fe<sub>2</sub>O<sub>3</sub> nanorods grown on the carbon fabric.

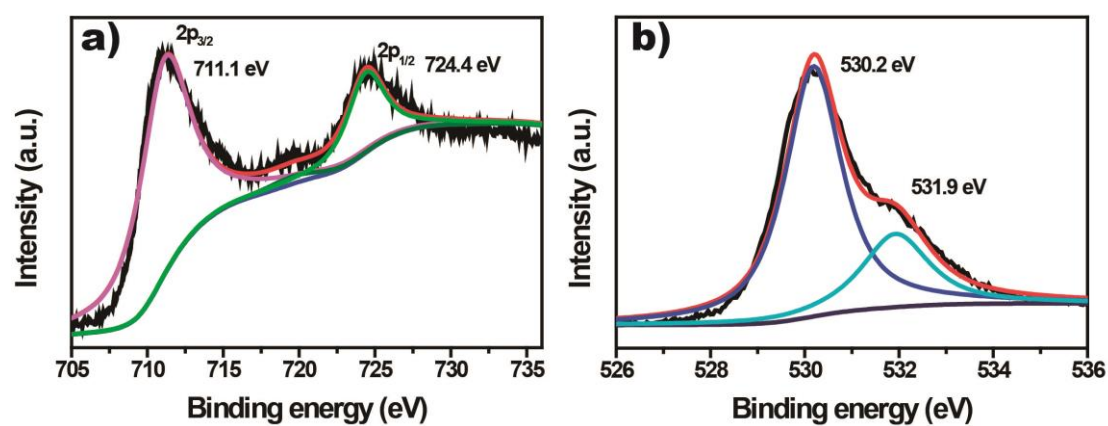


**Figure S10.** XRD of the as-prepared Fe<sub>2</sub>O<sub>3</sub> electrode.

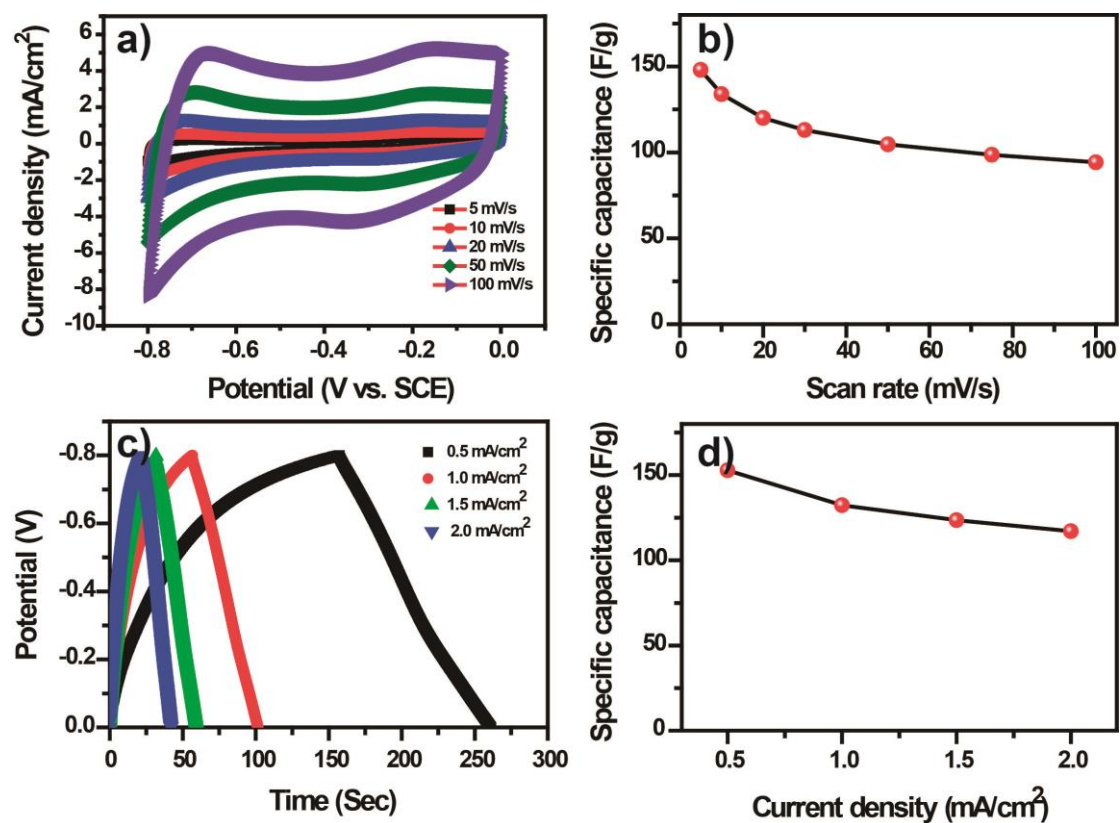




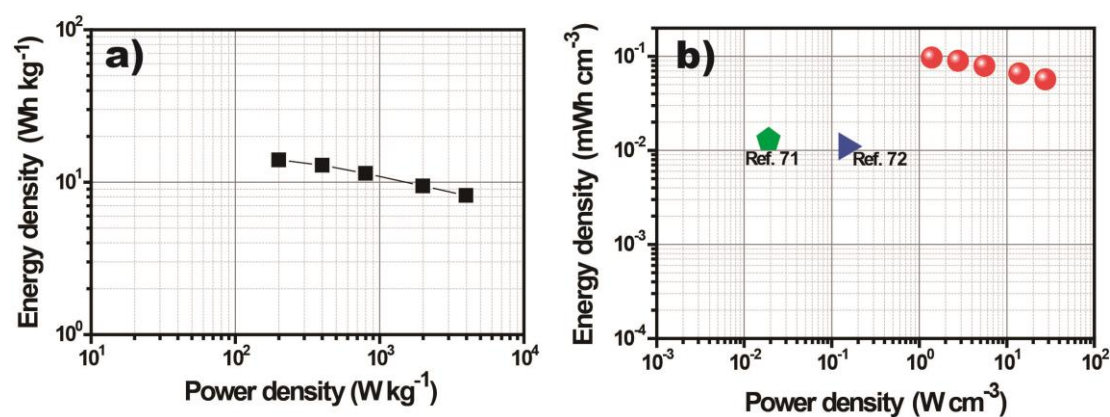
**Figure S11.** TEM images of  $\text{Fe}_2\text{O}_3$ .



**Figure S12.** XPS in the region of Fe 2p (a) and O 1s orbits (“black” represents the raw data, and the red line is the total fitted curve).



**Figure S13.** Electrochemical performance of the  $\text{Fe}_2\text{O}_3$  electrode. **a)** CV curves at different scan rates in 1.0 M  $\text{Na}_2\text{SO}_4$  electrolyte; **b)** Mass capacitance of  $\text{Fe}_2\text{O}_3$  electrode calculated from CV curves as a function of scan rate; **c)** Galvanostatic charge-discharge curves at different current densities; **d)** Mass capacitance of  $\text{Fe}_2\text{O}_3$  electrode calculated from GCD curves as a function of scan rate.



**Figure S14.** Ragone plots of the solid-state ASC device.

## References

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